Technoeconomic Analysis of an Artificial Photosynthesis Fuel Plant Supplied by Raw Biogas

Authors:

Jeffery B. Greenblatt^{1,2}, Ling Jin¹

¹Energy Analysis and Environmental Impacts Division, Lawrence Berkeley National Laboratory

²Now at Emerging Futures, LLC, Berkeley, CA

Energy Analysis and Environmental Impacts Division Lawrence Berkeley National Laboratory

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Jeffery Greenblatt^{1,2}* and Ling Jin¹

¹Lawrence Berkeley National Laboratory, Berkeley, CA 94720 ²Now at Emerging Futures LLC, Berkeley, CA 94710

* Correspondence to jeff@emerging-futures.com

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Overview

The objective of this collaboration between the Joint Center for Artificial Photosynthesis (JCAP) and Sempra Energy is to work towards development of a comparative analysis of net life-cycle energy use of a renewable fuel plant at pilot scale using water (H_2O), carbon dioxide (CO_2), sunlight and grid electricity as inputs. The work builds upon existing and ongoing analysis at JCAP examining hydrogen and hydrocarbon fuel production systems. We define "pilot scale" as a total fuel output of ~200 m³/hr., equivalent to ~1-2 MW continuous output (depending on the distribution of products). Note that we assume plant operation during non-sunlit hours using low-carbon grid electricity to maximize plant capacity factor and utilization of expensive capital.

Electrochemical (EC) or photoelectrochemical (PEC) CO₂ reduction using a copper catalyst results in a variety of fuel products, including hydrogen (H₂), carbon monoxide (CO), methane (CH₄), ethylene (C₂H₄), other hydrocarbons and oxygenates (e.g., ethanol, propanol, acetaldehyde, formate ion/formic acid, etc.) (e.g., Hori et al., 1994, 2003), as well as oxygen (O₂). All of these products have some commercial value and will result in multiple revenue streams, depending on purity. Figure 1 provides a high-level overview of a hypothetical renewable fuels plant.

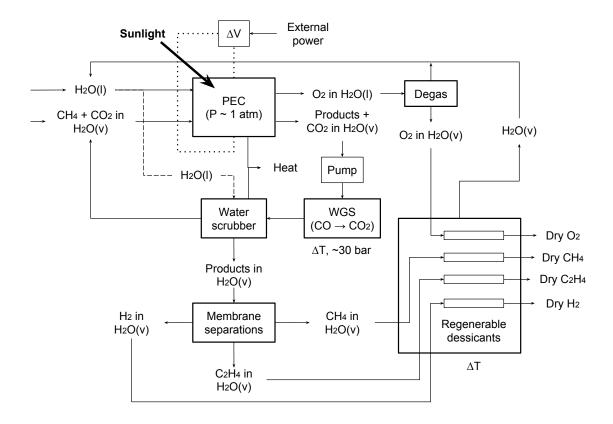


Figure 1. Overview diagram of renewable fuels plants

An important sustainability consideration is the source of CO_2 . Here we assume that this CO_2 is biogenic in origin and is supplied from raw biogas, which is composed of $\sim 50\%$ CO_2 and $\sim 50\%$ CH_4 by volume. Because CH_4 is a major product from our plant, we further assume that the raw biogas (once impurities such as hydrogen sulfide, ammonia, chlorine and siloxanes are removed) is passed into our renewable fuel plant without first separating the CH_4 . H_2O is the other reagent and is assumed to be provided from a municipal source at very low cost, and deionized prior to utilization.

The heart of the plant is the PEC reactor, which converts sunlight (or externally-supplied power, shown in the diagram as ΔV), CO₂ and H₂O into various reduced products plus O₂, along with heat that must be rejected. The PEC reactor is shown in more detail in Figure 2, while Figure 3 shows a photograph of an actual working prototype device.

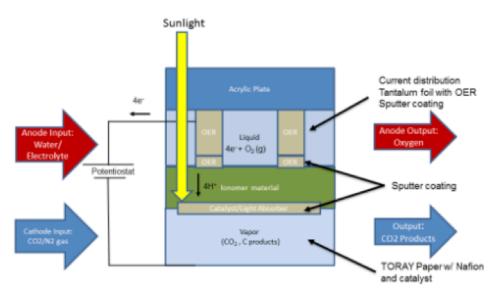


Figure 2. PEC device diagram

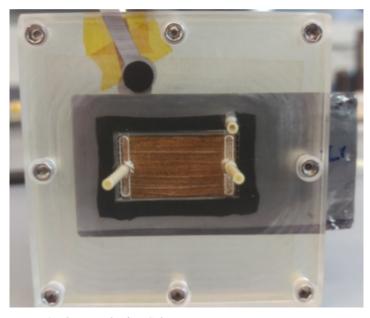


Figure 3. Photograph of PEC device prototype

The PEC design consists of two half reactors (cathode and anode). The cathode reactor employs a gas diffusion electrode to maximize the amount of CO_2 contacting the copper catalyst. (If CO_2 is dissolved in H_2O , on the other hand, its concentration under ambient conditions would be limited to $\sim 0.3\%$.) The light absorber material is assumed to be in intimate physical contact with the catalyst. The anode catalyst is iridium coated on laser-etched tantalum micro-wire, while the cathode catalyst is coated on Toray carbon paper.

The anode reactor can operate in the liquid or gaseous phase to provide H_2O as the reagent. While gas phase CO_2 reduction has not yet been explored at JCAP, it has been successfully demonstrated for H_2/O_2 production, which is considered a more demanding case because of the generally higher current densities involved.

An electrolyte-saturated Nafion® (or similar) membrane is required for both liquid and gaseous phase operation to facilitate ion transport while serving as a physical barrier between cathode and anode reactions. (For gas phase operation, the cathode reagent stream must be humidified to prevent membrane drying.)

The O_2 is assumed to be produced without significant impurities since it is the sole product formed on the anode side of the reaction, and product crossover is assumed to be minimal (< 1%).

The remainder of the renewable fuels plant consist of the following elements:

1. On the cathode side:

- a. Water-gas shift (WGS) reactor to convert CO (which is otherwise difficult to separate from other products) into H_2 plus additional CO_2 . This device requires elevated temperature ($\Delta T \sim 300$ °C).
- b. Water scrubbing (or membrane separation) of CO₂ from other gases
- c. Membrane separation of remaining fuels into components: H₂, C₂H₄, CH₄ and other gases, along with gas compression prior to each separation step. H₂ is assumed to be separated first, as it is straightforward to remove at high efficiency via cellulose acetate or other polymers. Separating C₂H₄ from CH₄ is considerably more challenging, and represents an area of active research. We discuss possible separation approaches below.
- d. Drying of resulting product gases using regenerative dessicants such as calcium chloride, magnesium sulfate or other salts, which are reactivated by mild heating (see Greenblatt et al., 2018).

2. On the anode side:

- a. Degassing of O₂ from H₂O liquid (if operated in liquid phase)
- b. Drying of O₂ (using a regenerative dessicant similar to above).

Note also that not all of the CO_2 is assumed to be reacted in the first pass through the PEC reactor, so recycling of this gas back through the reactor is essential.

Separation of gases is a challenge (e.g., Greenblatt et al., 2018), but there are established approaches for H₂ and CO₂, which can easily be separated from other gases using a variety of membranes (e.g., Baker, 2012), and for CO₂, scrubbing with either amines (Rochelle, 2009) or water (Shah and Nagarsheth, 2015; Walozi et al, 2016) is also possible, whereby the gas mixture is passed through a solvent reservoir that preferentially dissolves CO₂, depleting it relative to other gases. Separation of C₂H₄ is far more challenging, and while approaches exist, they are still very much at a research stage (e.g., Kang et al., 2006; Pan et al., 2015; Pan et al., 2016).

Plant Design Parameters

We assume that a large biogas plant that is similar to the Zero-Waste Energy Development Company (ZWEDC) facility located in San Jose, California supplies biogas to the renewable fuels plant. The biogas from the ZWEDC plant consists of $\sim 50\%$ CO₂ and $\sim 50\%$ CH₄, with a CO₂ flow rate of ~ 200 m³/h or 8,460 mol/h. The total flow rate of the raw biogas is therefore ~ 400 m³/h or 16,920 mol/h. If we assume that H₂O is consumed at a 2:1 stoichiometry with CO₂, there is an equivalent H₂O vapor flow rate of 400 m³/h or 16,920 mol/h. However, note that the consumption of H₂O will vary depending on the product distribution, which is driven by the type of copper catalyst chosen; see Table 1:

Table 1. Distribution of products and reagents for various copper catalysts

	Cu	Cu(100)	Cu(711)	Cu(511)	Cu(311)	Cu(111)
Moles produced (or consumed) per mole of CO ₂ consumed						
Methane (CH ₄)	44.4%	32.2%	5.9%	15.3%	48.5%	73.8%
Ethylene (C ₂ H ₄)	22.7%	28.6%	39.4%	34.8%	21.4%	8.8%
Carbon monoxide (CO)	6.9%	3.8%	5.2%	10.2%	14.0%	40.8%
Hydrogen (H ₂)	109.4%	28.9%	73.7%	96.9%	71.7%	103.9%
Acetaldehyde	1.2%	1.4%	1.1%	1.5%	1.2%	2.7%
Ethanol	1.2%	1.6%	1.3%	2.5%	0.7%	0.6%
Propionaldehyde	1.4%	1.3%	2.8%	1.8%	1.4%	0.4%
Allyl alcohol	0.2%	0.1%	0.2%	0.2%	0.0%	0.1%
Propanol	0.3%	0.1%	0.4%	0.4%	0.2%	0.0%
Formate ion	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Acetic acid	0.0%	0.1%	0.1%	0.1%	0.1%	0.2%
Inerts (assumed)	3.8%	2.0%	2.7%	3.3%	3.2%	4.7%
Total fuels (including inerts)	191.4%	100.0%	132.8%	166.9%	162.5%	236.1%
O ₂ produced	229.0%	181.0%	190.3%	209.3%	215.8%	257.5%
H ₂ O consumed	255.3%	162.8%	181.4%	215.0%	221.1%	278.4%
Other parameters						
Combustion energy of fuels (kJ HHV*/mol CO ₂)	1103	845	916	1017	1028	1242
Solar area required (m ²)	35,493	27,212	29,474	32,751	33,079	39,997
Length of square side (m)	188	165	172	181	182	200
Peak solar output (MW)	2.59	1.99	2.15	2.39	2.41	2.92
Peak electrical input (MW)	5.18	3.97	4.30	4.78	4.83	5.84
Daily electrical energy (GJ)	324	249	269	299	302	365
Total gas piping needs (mol per mol CO ₂ input)	8.76	6.44	7.04	7.91	7.99	9.72

Fuel output relative to Shaner et al. (2016) (207,000 mol/h)	7.82%	4.09%	5.43%	6.82%	6.64%	9.65%
Total gas piping need relative to Shaner et al. (2016)	68.5%	26.3%	38.2%	54.0%	53.1%	93.8%
Compressor/condenser gas volume relative to Shaner et al. (2016)	40.7%	15.6%	23.0%	32.5%	31.8%	57.3%

^{*} HHV = higher heating value. Based on data from Hori (1994, 2003) and calculations in Greenblatt et al. (2018)

Following Sathre et al. (2016), we assume peak insolation of 1,000 W/m² and 10% loss each due to dust, cell degradation and inactive panel area, resulting in 729 W/m² delivered to the PEC system. Assuming 10% solar-to-fuel (STF) conversion efficiency, the total solar power converted into chemical fuels (on a higher heating value or HHV basis) is 73 W/m².

The area required to supply this energy will vary with the overall fuel output and distribution of products (assuming the total STF efficiency is the same in each case, which may not necessarily be true in practice). This is illustrated in Table 1 where the combustion energy of the fuels produced per mole CO₂ consumed varies between 845 and 1242 kJ. This results in a variation in the required area of the solar collector of between ~27,000 and ~40,000 m², or a linear dimension of between 165 m and 200 m. For simplicity, we take an average value of 181 m as our reference case.

To maximize plant utilization, we assume that during off-peak solar conditions as well as at night, an external voltage is applied to drive the reaction. The power required is identical to that supplied by solar energy, divided by the electrical-to-chemical conversion efficiency, here assumed to be 50%, based on \sim 60% HHV efficiency for H_2O electrolysis systems (Eichman et al., 2016). As a result, electricity input is between 4.0 and 5.8 MW. Assuming solar energy is available 27.6% of the time (Sathre et al., 2016), required grid-supplied electricity is between 249 and 365 GJ/day.

Some additional CO₂ is produced in the WGS reactor, which converts CO and H₂O into CO₂ and H₂. The percentage of CO produced is listed in Table 1 and for simplicity, we take an average value of 13% as our reference case. The CO₂ is assumed to be separated with 90% efficiency and recycled back to the PEC cell. Assuming p = fraction of additional CO₂ produced from the WGS, and q = recycling efficiency, for 1 mol of CO₂ from biogas, the equilibrium recycled CO₂ = pq/(1-pq) mol. Therefore, the total input CO₂ will be 1/(1-pq) mol. Currently, we are using p = 0.13 and q = 0.9 for a total input CO₂ to the PEC of ~1.1 times the amount of CO₂ in the biogas stream.

Catalyst loadings (mass per unit area) are needed to calculate total catalyst costs. JCAP researchers report utilization of 1-10 g/m² of sputtered copper for the cathode reactor. For the anode reactor, 100 nm of sputtered iridium is currently used; at a density of 22.56 g/cm³, the loading is 2.256 g/m². By comparison, catalyst loadings for PEC H₂O-splitting systems in Shaner et al. (2016) were assumed to be much lower: 0.01-0.1 g/m² platinum and 0.02-0.2 g/m² iridium oxide (equivalent to 0.017-0.17 g/m² iridium).

Financial Assumptions

Following Sathre et al. (2014, 2016) we assume a 40-year facility life and 10-year panel life (for active components) as our base case. The discount rate is assumed to be 12%/yr and inflation rate is 2%/yr following Shaner et al. (2016). The financial assumptions and cost related parameters used in this study are summarized in Table 2.

Table 2. Financial assumptions and capital and operational expense parameters

Parameter	Value	Reference			
Financial assumptions					
Plant lifetime	40 years	Sathre et al. 2014, 2016			
Panel lifetime	10 years	Sathre et al. 2014, 2017			
Discount rate	12%	Shaner et al. 2016			
Inflation rate	2%	Shaner et al. 2016			
Land cost	\$500/acre	DOE, no date.			
Installation cost	15% of capital cost	Shaner et al. 2016			
PEC (Components (\$ per m2	of insolation area)			
Window (antireflection-coated glass)	5	Shaner et al. 2016			
Chassis (polypropylene)	33	Shaner et al. 2016			
Semiconductors (crystalline Si, 16% S-E)	48	Shaner et al. 2016			
Catalysts (platinum, iridium oxide)	81	Computed from this study			
Membrane (Nafion®, 5 mil)	50	Shaner et al. 2016			
PEC cell assembly labor	10	Shaner et al. 2016			
Heat exchangers	0.4	Shaner et al. 2016			
Control system	5.4	Shaner et al. 2016			
Panel mounting materials	29	Shaner et al. 2016			
Other balance of system	56	Shaner et al. 2016			
Other system capital costs (\$ per m2 of insolation area unless otherwise specified)					
Condenser	5.3	Shaner et al. 2016 and scaled by gas quantity of this study			
Compressor	0.1	Shaner et al. 2016 and scaled by gas quantity of this study			
Pipling (PVC)	1.9	Shaner et al. 2016 and scaled by gas quantity of this study			
Membrane separation	40	Greenblatt et al. 2018			
Water-gas-shift system	\$45/(m3/h of CO)	Torkelson et al. 2008			

Revenue Related Data

We assume that revenue will come from selling products including O_2 , H_2 , C_2H_4 , and CH_4 mixed with other hydrocarbons (pipeline gas). The value of CO_2 avoided (from using biogas- rather than fossil-based fuels) is also included. Relevant reference prices along with high and low estimates are listed in

Table 3.

Table 3. Price assumptions of products

	Price (\$/kg)			
Gas	Low	Reference	High	Reference and notes
O ₂	0.1	0.2	1.0	Values are composites of several estimates: Advanced Gas Technologies (2014), Chemicool (2018), Liquid Air Energy Network (2013), Praxair (no date), Quora (2012) and SpaceX (2016).
H ₂	2.0	3.0	14.0	Low and reference value are from Eichman et al. (2016); high value (actually \$13-16/kg) is from Satyapal (2017).
CH ₄ mixture	0.142	0.158	0.174	Natural gas futures through 2028 from CME Group (2018a); assumed ±10% for high/low bounds.
C ₂ H ₄	0.441	0.490	0.539	Futures through 2020 from CME Group (2018b); assumed ±10% for high/low bounds.
CO ₂	0.04	0.15	0.30	The reference value from California Public Utilities Commission (2017) and represents a 2030 price for California. The low value is from Worland (2018). The high value is assumed to be twice the reference value.

For this analysis, we compute the levelized cost for the fuel products normalized by the quantity of CO₂ input. We do this instead of normalizing to a single fuel because the system produces multiple products. After we determine the levelized cost, we compare it with the estimated revenue from all products.

Capital Cost Items

Land cost is set to \$500/acre according to the H2A model default (DOE, no date). This value can change with locations. Land requirement is proportional to panel area with a 4.6:1 ratio based on a similar design in Sathre et al. (2016).

The component capital costs (in 2014 dollars) are divided into two categories:

- Component with insolation area-dependent costs. These costs are associated with materials needed to build the panel, balance of system (BOS), etc. and are closely coupled to STF ratio.
- Component with costs that scale with gas quantities.

PEC Components and Related Costs

Costs are defined in terms of 2014 dollars per m² of insolation area. Initial values are taken from Shaner et al. (2015) except for catalysts (see Table 2).

Catalysts: Given the loadings calculated earlier, we utilize current commodity metal prices to determine catalyst costs per unit area. Copper currently costs ~\$7/kg (InfoMine, Inc., 2018); at

 10 g/m^2 , the cost is $\sim \$0.07 \text{ per m}^2$ for the cathode. Iridium, on the other hand, costs $\sim \$36,000/\text{kg}$ (Quandl, 2018), so with a loading factor of 2.256 g/m², the cost is $\$81.22/\text{m}^2$ for the anode. In total, the combined (cathode + anode) catalyst cost is $\$81.29/\text{m}^2$. This value is about ten times higher than the value used in Shaner et al. (2016) because the layers are assumed to be thicker.

Other System Capital Costs

Other costs associated with system-wide or process-based capital are mostly determined by gas quantities that are constants given that the input biogas stream is assumed to be fixed.

For the compressors, water condenser, and PVC piping, we use the costs given in Shaner et al. (2016) and assume they linearly scale with the gas quantities.

For PVC piping, we assume that the biogas input stream contains 50 mol% CO_2 and 50 mol% CH_4 , e.g., 1 mol CO_2 and 1 mol CH_4 . The system produces between 1.0 and 2.4 mol of fuels per mol CO_2 input, depending on the catalyst case (see Table 1). Between 1.6 and 2.8 mol of H_2O vapor must also be supplied to the device, with 1.8 to 2.6 mol O_2 produced. Therefore, the total piping needed is 6.4 to 9.8 times that of the H_2 system, which only produces 1 mol H_2 as output, since the product O_2 is discarded and the supplied H_2O , being liquid, requires much smaller pipes. However, the total capacity needed is lower than in Shaner et al.: compared with their output of 10,000 kg/day $H_2 = 207,000$ mol/h, we produce between 8,460 and 19,970 mol/h of products, or 4.1% to 9.6% of their output. Thus, total piping needs are between 6.4 × 4.1% = 26% and 9.8 × 9.6% = 94% of the gas volume in Shaner et al. Summary calculations for each catalyze case is shown in Table 1. For simplification purposes, we take the average across the six catalyst cases of 56% as a reference value.

For condenser and compressors, we will have between 2.0 and 3.4 mol of fuel (1 mol from biogas, and 1.0 to 2.4 mol from the PEC system), plus between 1.8 and 2.6 mol of O_2 , so the total need is between $3.8 \times 4.1\% = 16\%$ and $5.9 \times 9.6\% = 57\%$. The average across six cases, 33%, is used as a reference value.

The WGS system has low cost compared to the membrane separation system. Currently we use \$45/(m³/h of CO) (from Torkelson et al. 2008) to derive capital costs. (Note this reference may have included operating costs as well.)

Capital costs for membrane separation systems are based on estimates compiled in Greenblatt et al. (2018) of \sim \$40/m² of membrane area. For the three separations involved (H₂, CO₂ and C₂H₄), we assume gas permeabilities of \sim 50, \sim 10 and \sim 0.1 Barrer, respectively (Sanders et al., 2013; Kang et al., 2006), initial pressures of 10 bar, and membrane thicknesses of 100 nm. The resulting membrane areas are 12, 81 and 1660 m², resulting in a total cost for all three membranes (dominated by the C₂H₄ membrane) of \$70,070. Note that the capital cost of the CO₂ membrane separation process is used in lieu of a CO₂ water scrubbing system estimate.

For product drying, we use the water condenser costs capital costs.

Finally, the installation labor is assumed to be 15% of the installed capital costs from all above (PEC related and other system capital costs).

Operating Cost Items

We assume that PEC active components (semi-conductors, catalysts, and membrane) will be replaced every 10 years following Sathre et al. (2014, 2016). This will incur material and installation costs at the time of the replacement. Installation labor costs are assumed to be 15% of the replaced capital. Other components are assumed to need no replacement over the system lifetime following Shaner et al. (2016). Annual operations and maintenance costs are assumed to be 3.2% of the total capital cost (2014 dollars) except for grid power to drive PEC.

We assume solar energy is available 27.6% of the time (on an annual basis), and grid electricity is used to drive electrolysis for the rest of the time. Assuming 50% of grid-to-fuel conversion efficiency, the grid electricity consumed is $(1 - 27.6\%) / 27.6\% / 50\% \times 10\% = \sim 0.5$ times the incident solar energy.

Levelized Cost

A standard discounted cash flow is applied to the system over the assumed plant lifetime. The capital expenditure is assumed to occur over a one year construction period. All the operating expenses and levelized annual costs are discounted to the year of construction. Replacement costs are included every 10th year. A pre-tax condition is assumed so that depreciation is not applied to capital assets. We also assume all the operation costs are inflating.

Results and Discussion

The reference case result shows a levelized cost of \$1.9 per kg of CO_2 input, of which \$0.7 is due to component costs, \$0.1 is due to labor, and \$1.1 is due to operational expenses (grid electricity consumption, operation and maintenance, replacement capital and labor). The grid electricity used for driving the PEC cell (\$0.7) accounts for \sim 64% of operational expenses.

We varied the assumed STF ratio and electricity price to explore how these parameters impacted the levelized cost. See Figure 4. Both parameters play important roles. At 10% STF, the levelized cost can be reduced to between \sim \$1.2 and \$1.4 per kg of CO₂ input at lower electricity prices (<\$0.025/kWh). If the STF can increase to 15%, the cost can be further reduced to \sim \$1.0 per kg of CO₂ input.

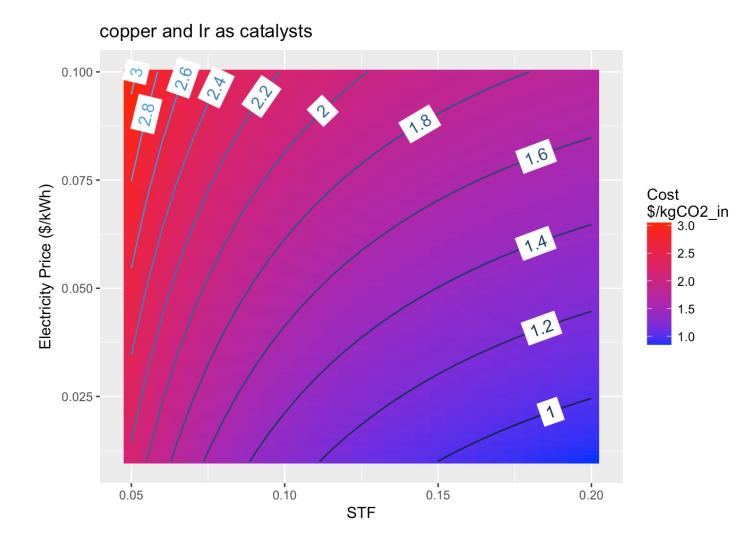


Figure 4. Sensitivity of levelized cost with STF ratio and electricity price

Revenue Analysis

As stated earlier, we assume that revenue will come from selling individual gaseous products including O_2 , H_2 , C_2H_4 and a mixture of CH_4 and other hydrocarbon (as pipeline gas). The market price (base case), low and high price bounds for each of the revenue streams are listed in

Table 3.

The distribution of fuel products depends on the copper catalyst used for the cathode. We modeled six cases [Cu, Cu(100), Cu(711), Cu(511), Cu(311), and Cu(111)] based on data from Hori et al. (1994) and (2003). The molar composition of fuel products (referred to as "PEC fuels" hereafter) are reported in Table 1. Assuming all the CO is converted to H₂ in the WGS process downstream of the PEC cell, these fuel products are aggregated into three revenue streams: C₂H₄, H₂, and CH₄ mixture. We further assume that 20% of the C₂H₄, 10% of the H₂, and all other hydrocarbons (including the biogas methane) are included in the CH₄ mixture, and that the CH₄ originally in the biogas is also included here. Another two revenue streams are the O₂ product and the CO₂ credits derived from hydrocarbon products (since they are not made from fossil sources).

We compute the revenue per kg of PEC fuels for each of the revenue streams across three price assumptions (high, reference and low values) for each of the six catalyst cases. These quantities are then normalized by the kg CO₂ consumed for comparison to the levelized cost. See Figure 5 and Figure 6.

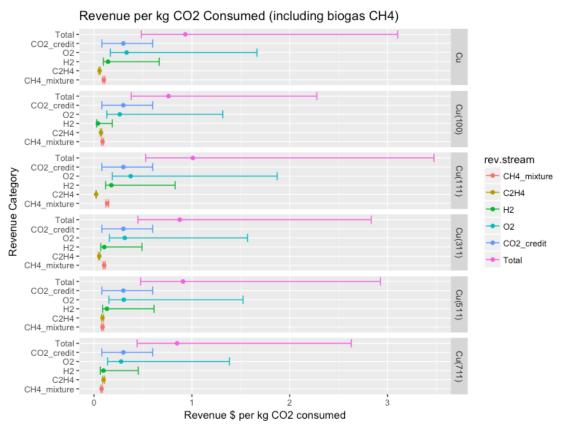


Figure 5. Revenue composition including biogas-derived CH₄ (absolute values)

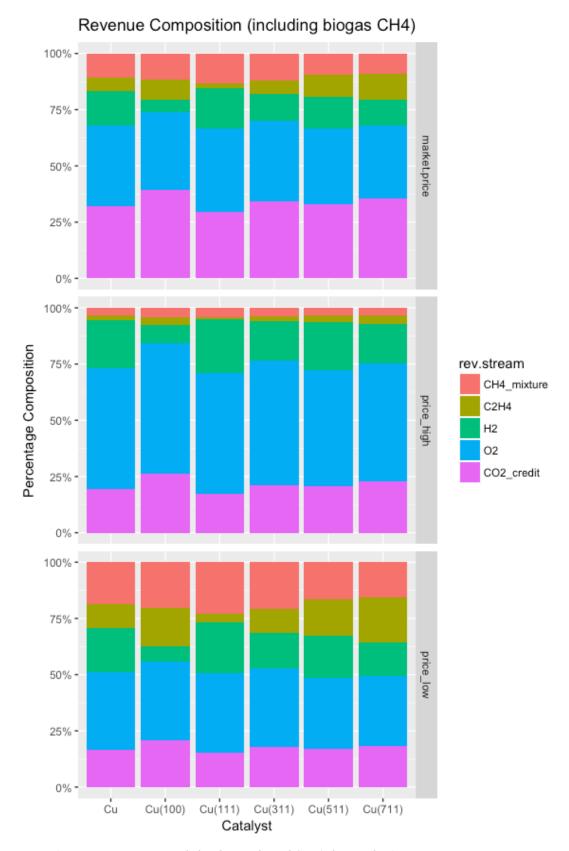


Figure 6. Revenue composition including biogas-derived CH₄ (relative values)

We observe that the C_2H_4 and CH_4 prices contribute the least to overall revenue, providing ~20% to overall revenue in the reference case, and <10% in the high price case. The products that dominate total revenues are H_2 , O_2 and CO_2 credits for the hydrocarbon fuels (dwarfing hydrocarbon prices in all but the low-price sensitivity case). Clearly, the inclusion of both H_2 and O_2 is critical to plant self-sufficiency.

While revenues are below the reference levelized cost in all reference price catalyst cases, in the high price sensitivity cases this cost is exceeded by a considerable margin for all catalysts, with the major contributors to the high prices from H_2 , O_2 and CO_2 credits. While the future price of H_2 may work against this trend (the U.S. Department of Energy expects the long-term H_2 price to fall to \sim \$2/kg, which sits at the low end of our range), the potentially higher future prices of O_2 (as energy costs increase) and certainly CO_2 paint a rosier economic picture.

Conclusions and Limitations

We have developed a preliminary technoeconomic analysis of a pilot-scale renewable fuel plant, built around a PEC reactor that converts H_2O , CO_2 , sunlight and grid electricity into various fuels and O_2 . The CO_2 is supplied as a component of treated biogas that contains ~50% CO_2 and ~50% CH_4 by volume. Our analysis was based on previous work modeling PEC hydrogen plants at scale (Sathre et al. 2014, 2016), hydrogen plant economic analysis (Shaner et al., 2016), PEC product separation (Greenblatt et al., 2018), and ongoing laboratory work building CO_2 reduction prototypes.

We find that STF efficiency and the price of off-peak electricity are critical input assumptions to plant cost-effectiveness. The precise choice of catalyst that controls product distribution is less important. Moreover, sales of products other than CH₄ and C₂H₄ fuel may command higher price premiums and thus make important contributions to overall revenue. We believe our modeling captures all important cost components, though overall uncertainties remain high. We conclude that while our results are potentially promising, further investigation and more detailed cost modeling is warranted to identify system designs and future price scenarios that might provide higher confidence in positive revenue flow.

References

Advanced Gas Technologies (2014). Oxygen Generators. http://adgastech.com/Products/Industrial-Gas-Generators/Oxygen-Generators. Accessed 16 February 2018.

Baker, Richard W., 2012. Chapter 8: Gas Separation. In: *Membrane Technology and Applications*, 3rd ed., West Sussex, United Kingdom: Wiley, pp. 325-378.

California Public Utilities Commission (2017). Proposed Reference System Plan, 18 September. http://cpuc.ca.gov/uploadedFiles/CPUCWebsite/Content/UtilitiesIndustries/Energy/EnergyPrograms/ElectPowerProcurementGeneration/irp/AttachmentA.CPUC_IRP_Proposed_Ref_System_Plan 2017 09 18.pdf.

Chemicool (2018). Oxygen Element Facts. https://www.chemicool.com/elements/oxygen.html. Accessed 5 April 2018.

CME Group (2018a). Henry Hub Natural Gas Futures Quotes.

http://www.cmegroup.com/trading/energy/natural-gas/natural-gas.html. Accessed 13 February 2018.

CME Group (2018b). Mont Belvieu Ethylene (PCW) Financial Futures Quotes. http://www.cmegroup.com/trading/energy/petrochemicals/mont-belvieu-ethylene-pcw-financial-swap-futures.html. Accessed 13 February 2018.

DOE (U.S. Department of Energy), no date. DOE H2A Analysis, Hydrogen and Fuel Cells Program. https://www.hydrogen.energy.gov/h2a_analysis.html. Accessed 20 April 2018.

Eichman, Joshua, Aaron Townsend, Marc Melaina (2016). *Economic Assessment of Hydrogen Technologies Participating in California Electricity Markets*, Technical Report NREL/TP-5400-65856, February. https://www.nrel.gov/docs/fy16osti/65856.pdf.

Greenblatt, J. B., Miller, D. J., Ager, J. W., Houle, F. A., and Sharp, I. D. (2018). The Technical and Energetic Challenges of Separating (Photo)Electrochemical Carbon Dioxide Reduction Products, *Joule* 2(3): 381-420. https://doi.org/10.1016/j.joule.2018.01.014.

Hori, Y., Wakebe, H., Tsukamoto, T., and Koga, O. (1994). Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media. *Electrochim. Acta* 39, 1833–1839.

Hori, Y., Takahashi, I., Koga, O., and Hoshi, N. (2003). Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes. *J. Mol. Catal. A.* 199, 39–47.

InfoMine, Inc. (2018). Copper Prices and Copper Price Charts, 11 April. http://www.infomine.com/investment/metal-prices/copper/. Accessed 12 April 2018.

Kang, Yong Soo, John Hak Kim, Jongok Won and Hoon Sik Kim, 2006. Chapter 16: Solid-State Facilitated Transport Membranes for Separation of Olefins/Paraffins and Oxygen/Nitrogen. In: *Materials Science of Membranes for Gas and Vapor Separation*, Yampolskii, Yu., I. Pinnau, B. D. Freeman, eds., Wiley, pp. 391-410.

Liquid Air Energy Network (2013). Chapter 6: Liquid air production and cost. http://liquidair.org.uk/full-report/report-chapter-six#ql-cost. Accessed 5 April 2018.

Pan, Yong, Huang Liu, Zhi Li, Bei Liu, Qinglan Ma, Guangjin Chen, Changyu Sun, Lanying Yang and Xueteng Gao, 2015. Ethylene Separation via Hydrate Formation in W/O Emulsions, *Energies* 8, 4871-4881; doi:10.3390/en8064871.

Pan, Yong, Chongzhi Jia, Bei Liu, Zhe Zhang, Xiongshi Tong, Hai Li, Zhi Li, Ronald Ssebadduka, Changyu Sun, Lanying Yang, Guangjin Chen, 2016. Separation of methane/ethylene gas mixtures efficiently by using ZIF-67/water-ethylene glycol slurry, *Fluid Phase Equilibria* 414: 14-22. https://doi.org/10.1016/j.fluid.2016.01.003

Praxair (no date). Price List - Praxair Distribution (T-0081). https://webcache.googleusercontent.com/search?q=cache:S3vVyVkuaT8J:https://wwwnet1.state.nj.us/treasury/dpp/ebid/Buyer/GetDocument.aspx%3FDocId%3D19789%26DocName%3DT008 1PriceList.pdf%26DocLoc%3D15+&cd=19&hl=en&ct=clnk&gl=us. Accessed 5 February 2018.

Quandl (2018). Rare Metals Prices and Charts, 12 April. https://www.quandl.com/collections/markets/rare-metals. Accessed 12 April 2018.

Quora (2012). How much does NASA pay per kg for hydrogen and oxygen in rocket fuel? https://www.quora.com/How-much-does-NASA-pay-per-kg-for-hydrogen-and-oxygen-in-rocket-fuel. Accessed 5 April 2018.

Rochelle, Gary T. (2009). Amine Scrubbing for CO₂ capture. *Science* 325 (5948): 1652-1654. DOI: 10.1126/science.1176731.

Sathre, R., C. D. Scown, W. R. Morrow, J. C. Stevens, I. D. Sharp, J. W. Ager, K. Walczak, F. A. Houle, J. B. Greenblatt (2014). Life-cycle net energy assessment of large-scale hydrogen production via photoelectrochemical water splitting, *Energy Environ. Sci.* 7: 3264–3278. DOI: 10.1039/C4EE01019A.

Sathre, Roger, Jeffery B. Greenblatt, Karl Walczak, Ian D. Sharp, John C. Stevens, Joel W. Ager III, Frances A. Houle (2016). Opportunities to improve the net energy performance of photoelectrochemical water-splitting technology, *Energy Environ. Sci.* 9: 803-819. DOI: 10.1039/c5ee03040d.

Satyapal, Sunita (2017). Hydrogen and Fuel Cells Overview, DLA Worldwide Energy Conference, National Harbor, MD, 12 April.

https://www.energy.gov/sites/prod/files/2017/06/f34/fcto-h2-fc-overview-dla-worldwide-energy-conf-2017-satyapal.pdf. Accessed 10 April 2018.

Shah, Divyang R., Hemant J. Nagarsheth (2015). Biogas Up Gradation using Water Scrubbing for its use in Vehicular Applications, *International Advanced Research Journal in Science*, *Engineering and Technology* 2(6): 46-48, June. DOI: 10.17148/IARJSET.2015.2611. http://www.iarjset.com/upload/2015/june-15/IARJSET%2011.pdf.

Shaner, M.R., Atwater, H.A., Lewis, N.S., and McFarland, E.W. (2016). A comparative technoeconomic analysis of renewable hydrogen production using solar energy, *Energy Environ*. *Sci.* 9: 2354-2371. DOI: 10.1039/C5EE02573G.

SpaceX, 2016. Making Life Interplanetary, 67th International Astronautical Congress, Guadalajara, Mexico, 27 September.

http://www.spacex.com/sites/spacex/files/making life multiplanetary 2016.pdf.

Torkelson, James, Neng Ye, Zhijiang Li, Decio Coutinho and Mark Fokema (2008). *Robust Low-Cost Water-Gas Shift Membrane Reactor for High-Purity Hydrogen Production from Coal-Derived Syngas*, Final Technical Report, Aspen Products Group, Marlborough, MA, August.

Walozi, Ronald, Betty Nabuuma, Adam Sebiti (2016). Application of Low Pressure Water Scrubbing Technique for Increasing Methane Content in Biogas, *Universal Journal of Agricultural Research* 4(2): 60-65. DOI: 10.13189/ujar.2016.040206. https://pdfs.semanticscholar.org/c60a/af2eab74fd7f6a011feb299891f9666372e4.pdf. Accessed 12 April 2018.

Worland, Justin (2018). Why College Republicans Think the GOP Should Act on Climate Change, 28 February. http://time.com/5176700/climate-change-college-republicans-donald-trump/.